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Functionalization of PEDOT by Click Chemistry and ATRP

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Abstract Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conductive polymer which has received increasing attention and many developments have been investigated. PEDOT has been applied in many different areas such as biosensors or polymer solar cells. This work presents a modification of PEDOT films through Click Chemistry with alkynes followed by activator regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) to develop PEDOT films with anti-fouling properties through application of a model system based on a crosslinked surface of polystyrene PS-N_3.

Introduction

Conductive polymers demonstrate a material sector of high interest which has been grown during the last few years. Many investigations have been conducted in order to develop the properties and application fields of conductive polymers.
One representative is poly(3,4-ethylenedioxythiophene) (PEDOT) which has become an important polymer in many applications such as in biosensors[1] or polymer solar cells[2].
The recently discovered PEDOT-N_3 films[3,4] can be modified through click chemistry with different alkynes, which leads to an open range of functional groups on the conductive polymer backbone especially applications in sensing control over fouling properties are essential.
Poly(ethylene glycol)methacrylate (PEGMA) is an important monomer for ATRP reactions which has shown good antifouling properties.
The presented study is focused on the application of ARGET ATRP to produce anti-fouling surfaces on PEDOT. Initital results on PEDOT and a model system is presented. "Grafting to" processes have earlier been tested and the presented work is compared to these results[3,5]. Furthermore a solution to confirm the validity of the method is an ARGET ATRP system with PEGMA, which has been tested. The presented work has been performed as a bachelor work at DTU.

Surface coating

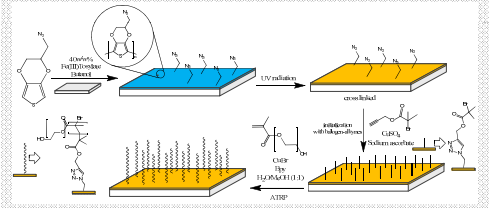

Figure 1. Functionalization of PEDOT-N_3 film with initiators, which subsequently was grafted through ATRP.

As already tested and reported the polymerization under normal ATRP conditions in an inert atmosphere has been successfully performed.
The advantage of ARGET ATRP is the use of a normal instead of an inert and closed atmosphere.
Due to its self- fluorescence it is difficult to determine the inhibition of protein adsorption of the PEDOT films using fluorescence measurements. For this reason a PS film modified with covalent bonded azide groups on the surface (PS-N_3) has been used for functionalization and further ARGET ATRP reaction.

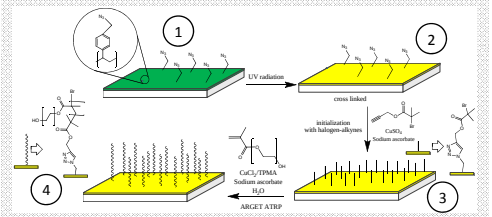

Figure 2. Preparation and functionalization of PS-N_3 film with initiator, which was subsequently grafted through ARGET ATRP

ATRP study

A well system has been designed to carry out the surface modification. This implies a non inert atmosphere, which should be suitable for ARGET ATRP.
The ARGET ATRP reaction in solution was tested to investigate the stability of the reaction in an open vessel.
The polymerization of PEGMA was performed through ARGET ATRP in water / methanol or pure methanol as solvents.

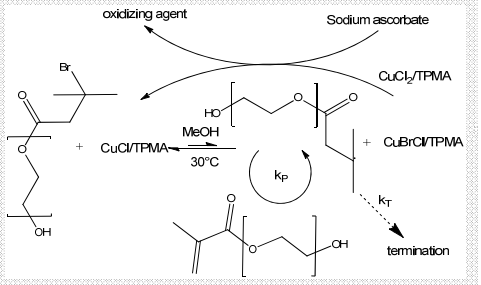

Figure 3. ARGET ATRP of poly(ethylene glycol) methacrylate (PEGMA) with Poly(ethylene glycol) methyl ether 2-bromoisobutyrate as initiator and $CuCl_2$ / Tris(2-pyridylmethyl)amine (TPMA) as a catalyst system and sodium ascorbate as a reducing agent

By varying of the molar ratios (monomer : Cu^{2+}, initiator : Cu^{2+} and ascorbic acid : Cu^{2+}) and the reaction time the most promising reaction in terms of a controlled reaction were investigated.
The reactions have been carried out in microplate wells under UV-VIS absorption measurements. Molecular weight distribution was determined by size exclusion chromatography (SEC).

PEGMA	Initiator	Cu^{2+}	TPMA	Sodium ascorbate	reaction time / min	solvent
1800	10	1	2,5	5	20 / 60	H_2O/MeOH (2:1) or MeOH
1800	10	1	2,5	10	20 / 60 / 120	H_2O/MeOH (2:1) or MeOH
1800	10	1	2,5	20	20 / 60 / 120	H_2O/MeOH (2:1) or MeOH
1800	10	1	2,5	40	20 / 60 / 120	H_2O/MeOH (2:1) or MeOH
7000	80	1	2,5	5	20 / 60	H_2O/MeOH (2:1) or MeOH
18000	90	1	2,5	20	20 / 60 / 90	H_2O/MeOH (2:1) or MeOH
18000	90	1	2,5	40	20 / 60 / 90	H_2O/MeOH (2:1) or MeOH

Table 1. Variation of molar ratios and reaction time for the ARGET ATRP reaction of PEGMA

SEC analysis show a relatively uncontrolled reaction. Polymers with a M_n=70000 have been observed and a polydispersity of 1,9 – 2,2. Many reactions result in polymer precipitation, which shows that the polymerization takes place. However a lack of control was investigated through a number of reactions. An impurity of dimer in the monomer is believed to be the source of crosslinking polymerization.
Since the scope is surface reactions and crosslinking systems tend to better antifouling properties the work was continued by introducing this reaction on the surface.

Model system for surface grafting

In the first step PS-N_3 films were inititalized through the reaction with prop-2-yn-1-yl 2-bromo-2-methylpropanoate , as an alkyne functional inititator which has been determined by FT- IR spectroscopical measurements.

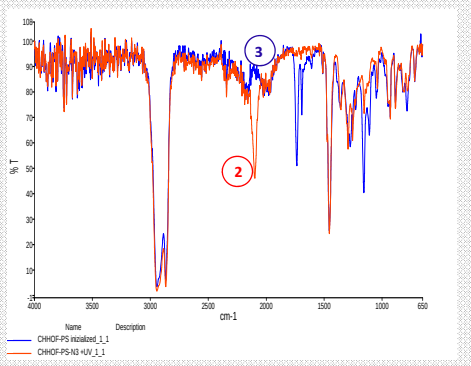

Figure 4. FT- IR spectroscopy of the polystyrene films before and after introducing of the ATRP initiator, red: not inizialized film, blue: inizialized film

The IR measurements clearly show the reaction of the azide groups with the initiator by disappearing of the band at 2100 cm^{-1}, which belongs to the free azides.

After the polymerization procedure the reaction mixtures have been exposed with fluorescent Albumin from bovine serum. The anti-fouling properties have been determined by fluorescence measurements.

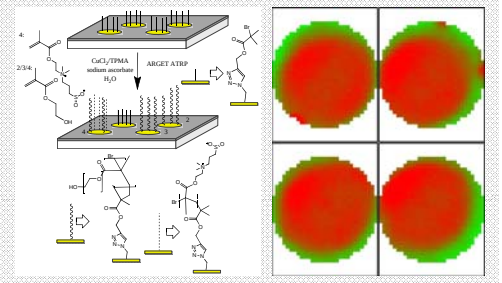

Figure 5. Left: ARGET ATRP system in microplate wells
Right: Fluorescence measurements after the samples have been exposed with the protein solution

To establish the surface changes of the polymerized films FT- IR spectroscopy has been used, which show no change in comparison to the initiated surface.

Conclusions

- Polymer synthesis with ATRP was not controlled
- Polymer precipitation leads to the assumption of cross linking reactions, which guide to a better suppresion of protein adsorption as already published
- Film initialization with "Click Chemistry" was successful
- Surface polymerization with ARGET ATRP was not successful
- No advantage in terms of protein adsorption

Perspective

The applied method has not provided surfaces with improved antifouling properties compared to the raw polymer surface. These results lead to a more detailed study with different types of monomers and varying of important reaction parameters such as reaction time, ratios between the reactants or the selection of a different system.
Furthermore the change from the PS model system to the PEDOT system is the next step. Investigations for the detection of the protein adsorption needs to be coducted.

References

(1) Luo, S.-chyang; Ali, E. M.; Tansil, N. C.; Yu, H.-hua; Gao, S.; Kantchev, E. A. B.; Ying, J. Y. *Society* **2008**, 8071-8077.
(2) Krebs, F. C.; Gevorgyan, S. a.; Alstrup, J. *Journal of Materials Chemistry* **2009**, *19*, 5442.
(3) Daugaard, A. E.; Hvilsted, S.; D.-K.; Hansen, T. S.; Larsen, N. B. *Macromolecules* **2008**, *41*, 4321-4327.
(4) Bu, H.-B.; Götz, G.; Reinold, E.; Vogt, A.; Schmid, S.; Blanco, R.; Segura, J. L.; Bäuerle, P. *Chemical communications* **2008**, 1320-2.
(5) Hansen, T. S.; Daugaard, A. E.; Hvilsted, Sø.,.; Larsen, N. B. *Advanced Materials* **2009**, *21*, 4483-4486.

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